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Description

This invention relates to aqueous liquid cleaning compositions, and in particular to liquid cleaning compositions containing enzymes.

Aqueous liquid enzymatic detergent compositions are well-known in the art. The major problem which is encountered with such compositions is that of ensuring a sufficient storage-stability of the enzymes in these compositions. There have already been various proposals for the inclusion of special stabilising agents in such enzymatic liquid cleaning compositions.

It has already been proposed, for example, to use boric acid or borates, with particular reference to sodium tetraborate, especially borax ($Na_2B_4O_7 . 10H_2O$) in aqueous liquid enzymatic cleaning compositions (see for example: Canadian Patent 947 213; French Patent 2 369 338; British Patent 1 590 445 and Japanese Patent Application 47/35,192). British Patent Application GB 2 021 142A discloses another stabilising system for enzymes, comprising a water-dispersible anti-oxidant and a water-soluble polyol.

It has now been found that an enzymatic liquid cleaning composition can be stabilised more effectively by the inclusion therein of an alkali metal pentaborate which may be used preferably in conjunction with an alkali metal sulphite and/or a polyol.

The pentaborate is used in an amount of more than 1.5% up to 15% by weight, preferably from 3—10% by weight of the composition. A preferred alkali metal pentaborate for use in the present invention is sodium pentaborate, $Na_2B_{10}O_{16} . 10H_2O$.

The alkali metal sulphite can be present in an amount of up to 15% by weight, preferably up to 10% by weight of the composition. A preferred alkali metal sulphite is sodium sulphite.

The polyols which can be used in the present invention contain only C-, H- and O-atoms. They are free from other (functional) substituting atoms such as N-, S- and the like. These polyols contain at least 2 hydroxy groups and may contain even up to 6 hydroxy groups. Typical examples of polyols particularly suitable for use in the present invention are diols such as 1,2 propane diol, ethylene glycol, erythritan, and polyols such as glycerol, sorbitol, mannitol, glucose, fructose, lactose, etc.

The polyol may be present in an amount of up to 15% by weight, preferably up to 10% by weight of the total composition.

Generally an effective stabilisation can be achieved with alkali metal pentaborate alone at a level of 6—15% by weight, preferably from 8—12% by weight, though levels of below 6% can also be effectively used in conjunction with an alkali metal sulphite and/or a polyol.

Advantageously the pH of the composition should preferably be kept at a level of about 7—8.2 to achieve the pest possible results. However, on varying the pentaborate:sulphite ratio the composition may have a pH above 8.2 with equally good results.

Generally a total amount of pentaborate, sulphite and/or polyol used in the composition not exceeding 20% by weight of the composition will be sufficient to achieve effective stabilisation as long as the total amount of stabilising system comprising the pentaborate is not below the 6% by weight level.

The advantage of pentaborate is that, when used at the level as herein defined, it generally provides a buffering effect on its own at the optimal pH condition to the liquid composition, which on dilution in use gives a sufficiently alkaline pH for optimal detergency, which effect is not achievable with other boron compounds such as a tetraborate or metaborate.

The stabilising system of the invention can be used in aqueous enzymatic liquid compositions, but has particular applicability to built liquid enzymatic detergent compositions.

The enzymes to be incorporated are selected from the group consisting of proteolytic, amylolytic and cellulolytic enzymes as well as mixtures thereof. They may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. However, their choice is governed by several factors, such as pH activity and/or stability optima, thermostability, stability versus active detergents, builders and so on. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases. Although the liquid compositions of the present invention may have a near-neutral pH value, the present invention is of particular benefit for enzymatic liquid detergents with a pH of between 7 and 8.2, especially those incorporating bacterial proteases of which the pH-optima lie in the range between 8.0 and 11.0, but it is to be understood that enzymes with a somewhat lower or higher pH-optimum can still be used in the compositions of the invention, benefiting from it.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of B. subtilis and B. licheniformis, such as the commercially available subtilisins Maxatase® (ex Gist-Brocades N.V., Delft, Holland) and Alcalase® (ex Novo Industri A/S, Copenhagen, Denmark).

As stated above, the present invention is of particular benefit for enzymatic liquid detergents incorporating enzymes with pH-activity and/or stability optima of above 8.0, such as enzymes also commonly called high-alkaline enzymes.

Particularly suitable is a protease, obtained from a strain of Bacillus, having maximum activity throughout the pH-range of 8—12, developed and sold by Novo Industri A/S under the registered trade name of Esperase®. The preparation of this enzyme and analogous enzymes is described in British Patent Specification No. 1 243 784 of Novo.

High-alkaline amylases and cellulase can also be used, e.g. alpha-amylases obtained from a special strain of B. licheniformis, described in more detail in British Patent Specification No. 1 296 839 (Novo).

The enzymes can be incorporated in any suitable form, e.g. as a granulate (marumes, prills, etc.), or as a liquid concentrate. The granulate form often has advantages.

The amount of enzymes present in the liquid composition may vary from 0.001 to 10% by weight, and preferably from 0.01 to 5% by weight, depending on the enzyme activity. The activity of proteolytic enzymes is usually expressed in Anson units or glycine units (1 Anson unit/g=733 glycine units/mg).

When the liquid enzymatic compositions of the invention are detergent compositions, these liquid detergent compositions comprise as a further ingredient an active detergent material, which may be anionic, nonionic, cationic, zwitterionic, amphoteric detergent material, alkali metal or alkanol amine soaps of a C_{10}—C_{24} fatty acid, or mixtures thereof.

Examples of anionic synthetic detergents are salts (including sodium, potassium, ammonium and substituted ammonium salts such as mono-, di- and triethanolamine salts) of C_8—C_{20} alkylbenzene-sulphonates, C_8—C_{22} primary or secondary alkane sulphonates, C_8—C_{24} olefin-sulphonates, sulphonated polycarboxylic acids, prepared by sulphonation of the pyrolyzed product of alkaline earth metal citrates, e.g. as described in British Patent Specification No. 1 082 179, C_8—C_{22} alkyl-sulphates, C_8—C_{24} alkylpolyglycol ether-sulphates (containing up to 10 moles of ethylene oxides); further examples are described in "Surface Active Agents and Detergents" (Vol. I and II) by Schwartz, Perry and Berch.

Examples of nonionic synthetic detergents are the condensation products of ethylene oxide, propylene oxide and/or butylene oxide with C_8—C_{18} alkylphenols, C_8—C_{18} primary or secondary aliphatic alcohols, C_8—C_{18} fatty acid amides; further examples of nonionics include tertiary amine oxides with one C_8—C_{18} alkyl chain and two C_{1-3} alkyl chains. The above reference also describes further examples of nonionics.

The average number of moles of ethylene oxide and/or propylene oxide present in the above nonionics varies from 1—30; mixtures of various nonionics, including mixtures of nonionics with a lower and a higher degree of alkoxylation, may also be used.

Examples of cationic detergents are the quaternary ammonium compounds such as alkyldimethyl ammonium halogenides, but such cationics are less preferred for inclusion in enzymatic detergent compositions.

Examples of amphotetic or zwitterionic detergents are N-alkylamino acids, sulphobetaines, condensation products of fatty acids with protein hydrolysates, but owing to their relatively high cost they are usually used in combination with an anionic or a nonionic detergent.

Mixtures of the various types of active detergents may also be used, and preference is given to mixtures of an anionic and a nonionic detergent. Soaps in the form of their sodium, potassium, or substituted ammonium salts such as of polymerized fatty acids, may also be used, preferably in conjunction with an anionic and/or a nonionic synthetic detergent.

The amount of the active detergent material may vary from 1 to 60%, preferably from 2—40% and especially preferably from 5—25%; when mixtures of e.g. anionics and nonionics are used, the relative weight ratio varies from 10:1 to 1:10, preferably from 6:1 to 1:6. When a soap is also incorporated, the amount thereof is from 1—40% by weight.

A particularly preferred active detergent mixture is that of a water-soluble anionic sulphonate or sulphate detergent and a nonionic detergent in a weight ratio of from about 6:1 to 1:1, with or without a soap in a ratio of up to 2:1 with respect to the nonionic detergent constituent.

The liquid compositions of the invention may further contain up to 60%, preferably 5—60% by weight of a suitable builder, such as sodium, potassium and ammonium or substituted ammonium pyro- and tripolyphosphates, ethylene-diamine tetraacetates, nitrilotriacetates, etherpolycarboxylates, citrates, carbonates, orthophosphates, zeolites, carboxymethyloxysuccinate, etc. Particularly preferred are the polyphosphate builder salts, nitrilotriacetates, zeolites, and mixtures thereof.

The amount of water present in the detergent compositions of the invention can vary from 5 to 70% by weight.

Other conventional materials may also be present in the liquid detergent compositions of the invention, for example soil-suspending agents, hydrotropes, corrosion-inhibitors, dyes, perfumes, silicates, optical brighteners, suds boosters, suds depressants such as protected silicone compounds, germicides, anti-tarnishing agents, opacifiers, fabric softening agents, oxygen-liberating bleaches such as hydrogen peroxide, sodium perborate or percarbonate, diperisophthalic anhydride, with or without bleach precursors, buffers and the like.

Though on using the invention, the pH of the final composition can be kept at near neutral, preferably from 7—8.2, the pH of the wash liquor, on using the composition, will be in the alkaline range of well above 8 at an in-use concentration of about 1%.

The invention will now be illustrated by way of the following examples:

Examples I—II

Three enzymatic liquids of the following compositions were prepared and stored at 37°C.

Composition (% by weight)	I	II	A
Na-dodecylbenzene sulphonate	6.0	6.0	6.0
Potassium soap	2.4	2.4	2.4
Nonionics	3.5	3.5	3.5
Sodium carboxy methylcellulose	0.1	0.1	0.1
Sodium toluene sulphonate	1.0	1.0	1.0
Sodium triphosphate	25.0	25.0	25.0
Fluorescent agent	0.1	0.1	0.1
Enzyme (Alcalase)*	9GU/mg	9GU/mg	9GU/mg
Sodium sulphite	—	4.5	9.0
Sodium pentaborate 10. H_2O.	9.0	4.5	—
Perfume+water	———	up to 100 %	———
pH of composition	7.35	8.15	8.4
pH (1% in distilled water)	8.76	8.82	9.7
pH (1% in very hard water)	8.50	8.40	8.6
% enzyme activity remaining after 2 weeks' storage at 37°C	50%	50%	0%

* 0.8% Alcalase of 1163 GU/mg (GU=glycine unit).

The enzyme stabilisation of the pentaborate formulation I and II according to the invention is evident.

Example III

The same base liquid detergent composition of Examples I and II was used in the following experiments wherein the stabilising system was varied:

System	(1)	(2)	(3)	(4)	(5)	(6)
Sodium tetraborate 5 . H_2O	4%	9%	—	—	—	—
Sodium pentaborate 10 . H_2O	—	—	4%	9%	—	—
Sodium metaborate 8 . H_2O	—	—	—	—	4%	9%
(a)+0% sulphite						
pH (composition)	8.61	8.51	7.76	7.19	10.27	11.36
pH (1% solution)	8.68	8.93	8.30	8.43	8.91	9.26
(b)+5% sulphite						
pH (composition)	8.58	8.49	7.66	7.01	9.80	11.34
pH (1% solution)	8.66	8.91	8.90	8.40	8.89	9.26
(c)+8% sulphite						
pH (composition)	8.60	8.52	7.65	7.16	10.26	11.48
pH (1% solution)	8.70	8.93	8.33	8.43	8.89	9.30

Comparison of enzyme activity after storage at 37°C

(1) (a) after two weeks — <10%
(2) (a) after two weeks — <10%
* (3) (a) after two weeks — 25%
* (4) (a) after two weeks — 40%
(5) (a) after two weeks — nil
(6) (a) after two weeks — nil

(1) (b) after two weeks — 50%
(2) (b) after two weeks — 55%
* (3) (b) after two weeks — 75%
* (4) (b) after two weeks — 100%
(5) (b) after two weeks — 10%
(6) (b) after two weeks — <10%

1(c) after three weeks — 70%
2(c) after three weeks — 60%
* 3(c) after three weeks — 70%
* 4(c) after three weeks — 100%
5(c) after three weeks — nil
6(c) after three weeks — nil

* The above results show the overall superiority of the pentaborate stabilising system according to the invention over other borate systems outside the invention.

Examples IV—V
The following compositions were prepared:

Compositions (% by weight)	IV	V
Alkylbenzene sulphonate	6.0	6.0
Triethanolamine soap	2.4	2.4
Nonionic	3.5	3.5
Sodium carboxy methylcellulose	0.1	0.1
Sodium toluene sulphonate	1.0	1.0
Sodium triphosphate	25.0	25.0
Fluorescent agent	0.1	0.1
Protease (Alcalase)*	9GU/mg	9GU/mg
Glycerol	3.0	—
Sodium sulphite	4.5	5.0
Sodium pentaborate 10 . H_2O	1.5	4.0
Water+perfume	——up to 100%——	
pH (composition)	7.92	7.70
pH (1% in distilled water)	8.40	9.00
pH (1% in hard water)	8.36	8.35
Enzyme activity remaining after 2 weeks' storage at 37°C	65%	75%
4 weeks' storage at 37°C	40%	65%

* 0.8% Alcalase of 1163 GU/mg.

From these results the beneficial effect of increased pentaborate level is clearly shown.

Example VI
Similar compositions were prepared using the following enzyme-stabilizing system:

Glycerol	5%	—
Sodium sulphite	—	7%
Sodium pentaborate $10H_2O$	2%	5%
pH (composition)	7.7	7.6
pH (1% in distilled water)	9.1	9.0
pH (1% in hard water)	8.4	8.4
Enzyme activity remaining after 4 weeks' storage at 37°C	50%	—
7 weeks' storage at 37°C	—	60%

Claims

1. Enzymatic liquid cleaning composition comprising:
(a) from 0.001 to 10% by weight of an enzyme selected from the group consisting of proteolytic, amylolytic and cellulolytic enzymes and mixtures thereof;
(b) from 0 to 15% by weight of an alkali metal sulphite;
(c) from 0 to 15% by weight of a polyol containing only C-, H- and O-atoms and having from 2 to 6 hydroxy groups; and
(d) water,
characterised in that it contains an alkali metal pentaborate in an amount of more than 1.5% up to 15% by weight.

2. A composition according to claim 1, characterized in that it contains from 3 to 10% by weight of said alkali metal pentaborate.

3. A composition according to claim 1 or 2, characterized in that said alkali metal pentaborate is sodium pentaborate ($Na_2B_{10}O_{16} . 10H_2O$).

4. A composition according to claim 1, 2 or 3, characterised in that it further comprises from 1—60% by weight of an active detergent material selected from the group consisting of anionic, nonionic, cationic, zwitterionic and amphoteric detergent materials, alkali metal or alkanolamine soaps of C_{10}—C_{24} fatty acids, and mixtures thereof; and from 0 to 60% by weight of a builder.

5. A composition according to claim 4, characterized in that it comprises:
(a) from 0.01 to 5% by weight of enzyme;
(b) from 0 to 10% by weight of alkali metal sulphite;
(c) from 0 to 10% by weight of polyol;
(d) from 2 to 40% by weight of active detergent material;
(e) from 5 to 50% by weight of builder, selected from the group of polyphosphate builder salts, nitrilotriacetates, zeolites and mixtures thereof;
(f) from 5 to 70% by weight of water; and
(g) more than 1.5 to 15% by weight of alkali metal pentaborate.

6. A composition according to claim 5, characterized in that said alkali metal sulphite is sodium sulphite and said polyol is glycerol.

7. A composition according to any of the above claims, characterised in that it has a pH of from 7 to 8.2.

8. A composition according to any of the above claims, characterised in that the total amount of pentaborate, sulphite, and/or polyol is from 6 to 20% by weight of the composition.

Patentansprüche

1. Enzymatische flüssige Reinigungsmittel-Zusammensetzung umfassend:
(a) 0,001 bis 10 Gew.-% eines Enzyms ausgewählt aus der Gruppe bestehend aus proteolytischen, amylolytischen und cellulolytischen Enzymen und Mischungen davon;
(b) 0 bis 15 Gew.-% eines Alkalimetallsulphits;
(c) 0 bis 15 Gew.-% eines Polyols enthaltend nur C-, H- und O-Atome mit 2 bis 6 Hydroxygruppen; und
(d) Wasser,
dadurch gekennzeichnet, daß sie ein Alkalimetallpentaborat in einer Menge von mehr als 1,5 Gew.-% bis zu 15 Gew.-% enthält.

2. Zusammensetzung gemäß Anspruch 1, dadurch gekennzeichnet, daß sie 3 bis 10 Gew.-% des Alkalimetallpentaborats enthält.

3. Zusammensetzung gemäß Anspruch 1 oder 2, dadurch gekennzeichnet, daß das Alkalimetallpentaborat Natriumpentaborat ($Na_2B_{10}O_{16} . 10H_2O$) ist.

4. Zusammensetzung gemäß Anspruch 1, 2 oder 3, dadurch gekennzeichnet, daß sie weiterhin enthält 1 bis 60 Gew.-% eines aktiven Detergensmaterials ausgewählt aus der Gruppe bestehend aus anionischen, nichtionischen, kationischen, zwitterionischen und amphoteren Detergensmaterialien, Alkalimetall- oder Alkanolamin-Seifen von C_{10}—C_{24} Fettsäuren, und Mischungen davon; und 0 bis 60 Gew.-% eines Aufbaustoffes.

5. Zusammensetzung gemäß Anspruch 4, dadurch gekennzeichnet, daß sie umfaßt:
(a) 0,01 bis 5 Gew.-% Enzym;
(b) 0 bis 10 Gew.-% eines Alkalimetallsulphits;
(c) 0 bis 10 Gew.-% Polyol;
(d) 2 bis 40 Gew.-% eines aktiven Detergensmaterials;
(e) 5 bis 50 Gew.-% Aufbaustoff, ausgewählt aus der Gruppe der Polyphosphat-Buildersalze, Nitrilotriacetaten, Zeoliten und Mischungen davon;
(f) 5 bis 70 Gew.-% Wasser und
(g) mehr als 1,5 bis 15 Gew.-% Alkalimetallpentaborat.

6. Zusammensetzung gemäß Anspruch 5, dadurch gekennzeichnet, daß das Alkalimetallsulphit Natriumsulphit und das Polyol Glycerin sind.

7. Zusammensetzung gemäß einem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß sie einen pH-Wert von 7 bis 8,2 aufweist.

8. Zusammensetzung gemäß einem der vorgehenden Ansprüche, dadurch gekennzeichnet, daß die Gesamtmenge an Pentaborat, Sulphit und/oder Polyol 6 bis 20 Gew.-% bezogen auf die Zusammensetzung ausmacht.

Revendications

1. Composition liquide enzymatique de nettoyage comprenant:

a) de 0,001 à 10% en poids d'une enzyme appartenant au groupe des enzymes protéolytiques, amylolytiques et cellulolytiques et leurs mélanges;

b) de 0 à 15% en poids d'un sulfite de métal alcalin;

c) de 0 à 15% en poids d'un polyol ne contenant seulement que des atomes C-, H- et O- et contenant de 2 à 6 groupes hydroxy, et

d) de l'eau,

caractérisée en ce qu'elle contient un pentaborate de métal alcalin en une quantité comprise entre 1,5% et 15% en poids.

2. Composition selon la revendication 1, caractérisée en ce qu'elle contient de 3 à 10% en poids dudit pentaborate de métal alcalin.

3. Composition selon l'une des revendications 1 et 2, caractérisée en ce que ledit pentaborate de métal alcalin est le pentaborate de sodium ($Na_2B_{10}O_{16} \cdot 10H_2O$).

4. Composition selon l'une des revendications 1 à 3, caractérisée en ce qu'elle comprend en outre de 1 à 60% en poids d'un matériau détergent actif, appartenant au groupe des matériaux détergents anioniques, non ioniques, cationiques, zwitterioniques et amphotères, des savons de métaux alcalins, ou d'alcanolamine, d'acides gras en C_{10}—C_{24}, et leurs mélanges; et de 0 à 60% en poids d'un élément structural.

5. Composition selon la revendication 4, caractérisée en ce qu'elle comprend:

a) de 0,01 à 5% en poids d'enzyme;

b) de 0 à 10% en poids d'un sulfite de métal alcalin;

c) de 0 à 10% en poids de polyol;

d) de 2 à 40% en poids d'un matériau détergent actif;

e) de 5 à 50% en poids d'un élément structural, appartenant au groupe des sels structuraux de polyphosphates, des nitrilotriacétates, des zéolites et de leurs mélanges;

f) de 5 à 70% en poids d'eau, et

g) de 1,5 à 15% en poids d'un pentaborate de métal alcalin.

6. Composition selon la revendication 5, caractérisée en ce que ledit sulfite de métal alcalin est le sulfite de sodium et le polyol est le glycérol.

7. Composition selon l'une des revendications 1 à 6, caractérisée en ce que son pH est compris entre 7 et 8,2.

8. Composition selon l'une des revendications 1 à 7, caractérisée en ce que la quantité totale de pentaborate, de sulfite et/ou de polyol est de 6 à 20% en poids par rapport à la composition.